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(54) Title: ELECTROLUMINESCENT DEVICES

(57) Abstract

An electroluminescent device has at least two active semiconductive conjugated polymer light emitting layers arranged be-
tween a cathode and an anode. The layers are arranged so that at least part of at least two layers lie in an emission zone of the
device.

Title of the Invention

ELECTROLUMINESCENT DEVICES

Field of the Invention

This invention relates to electroluminescent devices and particularly to such devices which have a conjugated polymer as the light emissive layer.

Background to the Invention

Electroluminescent devices of the type with which the present invention is concerned are described for example in PCT/WO90/13148. Reference may also be made to articles by Burroughes et al in Nature (1990) 347,539 and by Braun and Heeger Applied Physics Letters (1991) 58,1982.

These devices offer potential as large-area flat-panel displays since they can be fabricated over large areas using solution-processing techniques. The basic structure of these electroluminescent (EL) devices comprises a polymer film sandwiched between two electrodes, one of which injects electrons, the other of which injects holes.

In the Nature reference the importance of balancing electron and hole injection rates through selection of charge injection electrodes is recognised. For these polymers, it is clear that injection and transport of electrons is less easy to achieve than for holes; this was indicated by the demonstration of improved device efficiencies when low work function metals such as calcium were used as the negative contact layer, as explained in the article in Applied Physics Letters. From photoluminescence studies it has been identified that an important non-radiative decay channel for excitons in these polymers is by exciton diffusion to charged defects which act as quenching sites. Metal injection electrodes can provide many defect states and efficiencies can

be raised substantially by introducing an additional layer
between the emissive (polymer) layer and the calcium
(electrode) layer. For this, a molecular semiconductor,
2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3, 4-oxadiazole
(butyl PBD) in a poly(methyl methacrylate) PMMA matrix has
been used. This layer served both to prevent exciton
migration to the metal contact and to enhance electron
injection. In this context, reference is made to
"Light-Emitting Diodes Based on Conjugated Polymers: Control
of Colour and Efficiency", P.L. Burn, A.B. Holmes, A. Kraft,
A.R. Brown, D.D.C. Bradley and R.H. Friend, Symposium N, MRS
Fall Meeting, Boston Dec. 1991, MRS Symposium Proceedings 247,
647-654 (1992).

As described for example in PCT/WO92/03490, the contents of
which are incorporated herein by reference, PPV can be
chemically-modified to control its bandgap. For example,
poly(2,5-dialkoxyphenylenevinylene) is red-shifted, by some
0.4eV, with respect to PPV. Copolymers of PPV and
poly(2,5-dimethoxy-p-phenylenevinylene), PDMeOPV, allow
fine-tuning of the band gap. Furthermore, controlled
elimination of precursor leaving-groups allows both red- and
blue- shifting of the gap with respect to that for PPV; the
latter is achieved by interruption of conjugation along the
chain by the presence of non-conjugated groups.

To date therefore it has been possible to have a limited
amount of control over the colour of light emitted from an
electroluminescent device using conjugated polymers. The
present invention seeks to provide an electroluminescent
device having a broader range of colour emission.

This has not been achieved in an EL device using conjugated
polymer layers and is not a simple matter since the inventors
have found that it requires that at least two conjugated
polymer layers be put down and be simultaneously excited to
emit radiation without one having a detrimental effect on the
other.

Reference is made to EP-A-0443861 to Sumitomo which discloses
electroluminescent devices made with two layers of conjugated
polymers. In this device, only one layer is excited to emit
radiation and the other layer is used as a charge transport
layer to enhance the transfer of charges into the light
emitting layer.

Summary of the Invention

According to one aspect of the present invention there is
provided an electroluminescent device comprising: a first
charge carrier injecting layer for injecting positive charge
carriers; a first layer of a semiconductive conjugated polymer
having a band gap selected such that when it is excited
radiation at a first wavelength is emitted; a second layer of
a semiconductive conjugated polymer having a band gap selected
such that when it is excited radiation at a second wavelength
is emitted; a second charge carrier injecting layer for
injecting negative charge carriers; and means to enable an
electric field to be applied across the said layers wherein at
least a part of each of the first and second layers is located
in an emission zone of the device, said emission zone
extending over a capture region of the device wherein positive
and negative charge carriers combine with one another to form
excitons and having a width characteristic of the distance
over which said excitons migrate before decaying radiatively,
such that on application of an electric field to the device
both of said first and second polymer layers are caused to
emit radiation at their respective wavelengths.

As mentioned above, it is not readily apparent from the work
which has already been published in relation to conjugated
polymers that it is possible to use a plurality of layers to
control the colour of emitted radiation.

The inventors have found that it is possible to define an
emission zone in which light is emitted through the radiative
decay of excitons. This zone has a width resulting from the

capture region of the device where excitons are formed and
which is also related to the diffusion characteristic of the
excitons. The width of the emission zone can be approximately
the same as that of the captive region or it can extend beyond
it where the excitons diffuse from it before decaying
radiatively. Thus, by ensuring that both the first and second
layers have parts lying in this characteristic width, excitons
will be present in both the layers and cause emission of
radiation from the first and second layers. The effect is
quite clearly ascertainable from the experiments discussed
herein but there are different theories which could be
developed to support the practical observations. One theory
discussed herein is that the characteristic diffusion length
for an exciton determines the critical width of the emission
zone but there are other possibilities. The inventors have
thus determined that it is possible to control the properties
of a multilayer electroluminescent device by selecting the
thicknesses of the polymer layers so that at least two layers
have parts in the emission zone. In one aspect, the invention
involves the use of several polymer layers with different band
gaps, with layer thicknesses selected to be smaller than or
comparable to, the width of the emission zone. This results
in excitons in two or more layers, and thus to light emission
from the two or more layers. This then gives light emission
with a broader spectral range than can be achieved with one
layer. This (together with a colour filter, if necessary) may
allow fabrication of a white light source.

Whatever the theory underlying the observed effect, the
experimental evidence is to the effect that the width of the
emission zone is of the order of 50nm. Thus, in the preferred
embodiment, the first layer has a thickness which is not
greater than 50nm. Of course, more than two such layers can
be provided depending on the required colour of emitted
radiation. Generally speaking the emission zone will extend
for a width not greater than 200nm, but this depends on the
nature of the polymer layers and charge carrier injection
layers.

The location of the emission zone with respect to the charge
carrier injection layers depends on the mobilities of
electrons and holes within the polymer layers and on the
injection functions and can be determined for each particular
case using the models discussed later.

In one embodiment there is a third layer of a semiconductive
conjugated polymer between said second polymer layer and said
second charge carrier injecting layer, the thickness of the
third polymer layer being not greater than 50 nm. The
emission zone can include part of two layers, part of one
layer and a complete other layer or parts of two layers and a
complete other layer.

The electroluminescent device can include an additional layer
of a conjugated polymer adjacent the second charge carrier
injecting layer which is not necessarily electroluminescent
but which instead functions as a barrier layer.

Preferably the second charge carrier injecting layer is
calcium and the first charge carrier injecting layer is
indium-tin oxide coated onto a glass substrate.

The term "conjugated polymer" used herein indicates a polymer
for which the main chain is either fully conjugated,
possessing extended pi molecular orbitals along the length of
the chain, or else is substantially conjugated, but with
interruptions to conjugation at various positions, either
random or regular, along the main chain. It includes within
its scope homopolymers and copolymers. The present invention
can utilise any conjugated polymer which is capable of forming
a thin electroluminescent film.

Particularly preferred conjugated polymers include
poly(p-phenylene vinylene)PPV and copolymers including that
polymer. Preferred features of the polymers used with the
respective layers are that they should be stable to oxygen,
moisture and to exposure to elevated temperatures, they should

have good adhesion to an underlying layer, good resistance to
thermally-induced and stress-induced cracking, good resistance
to shrinkage, swelling, re-crystallisation or other
morphological changes. Moreover, the polymer film should be
resilient to ion/atomic migration processes, for example by
virtue of a high crystallinity and high melting temperature.
Particularly preferred polymers are discussed in the
literature referred to above, particularly in PCT/WO90/13148
the contents of which are herein incorporated by reference. A
particularly suitable polymer is a poly(2,5-dialkoxyphenylene-
vinylene). Examples are MEHPPV, poly(2-methoxy-5-
(2-methylpentyloxy)-1,4-phenylenevinylene),
poly(2-methoxy-5-pentyloxy-1,4-phenylenevinylene), and
poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene), or other
poly(2,5-dialkoxyphenylenevinylenes) with at least one of the
alkoxy groups being a long solubilising alkoxy group, linear
or branched. Other suitable conjugated polymers can also be
selected from the poly(alkylthienylene)s. One example is
poly(3-dodecylthienylene).

The film of conjugated polymer is preferably a film of a poly(p-phenylenevinylene) [PPV] of formula
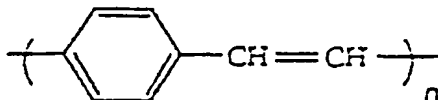
wherein the phenylene ring may optionally carry one or more substituents each independently selected from alkyl (preferably methyl), alkoxy (preferably methoxy or ethoxy) or any other substituent which maintains electroluminescent properties in the conjugated polymer.

Any poly(arylenevinylene) including substituted derivatives thereof or any poly(arylene) is also suitable. Throughout this specification the term "arylene" is intended to include in its scope all types of arylenes including heteroarylenes as well as arylenes incorporating more than one ring structure including fused ring structures.

Other conjugated polymers derived from poly(p-phenylenevinylene) are also suitable for use as the polymer film in the EL devices of the present invention. Typical examples of such derivatives are polymers derived by:

(i) replacing the phenylene ring in formula (I) with a fused ring system, e.g. replacing the phenelene ring with an anthracene or naphthalene ring system t. give a structure such as:-

or alternative linkage arrangements which maintain the electroluminescent properties in the conjugated polymer.
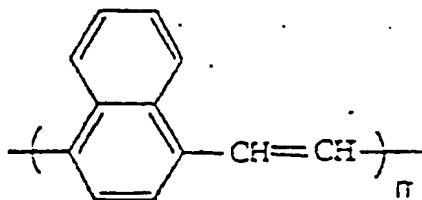
These alternative ring systems may also carry one or more substituents of the type described above in relation to the phenylene ring.

(ii) increasing the number of vinylene moieties associated with each phenylene ring (or each of the other alternative ring systems described above in (i) to give structures such as:-

or alternative linkage arrangements which maintain the electroluminescent properties in the conjugated polymer
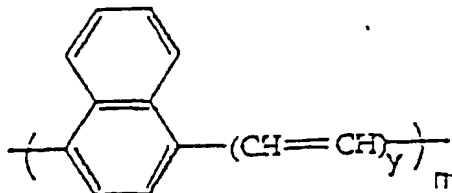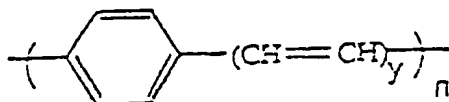
where y represents 2, 3, 4, 5, 6, 7,......

Once again, the ring systems may carry the various
substituents described above.

These various different PPV derivatives will possess different
semiconductor energy gaps. The ordering of the layers within
the electroluminescent device is affected by the individual
bandgaps. The layers should be ordered so that there is no
charge trapping at the boundaries between layers.

Other polymers which are particularly suitable for use in the
present invention are the semiconductive copolymers discussed
in PCT/WO92/03490, the contents of which are herein
incorporated by reference. In a preferred embodiment, the
copolymer is a conjugated poly(arylenevinylene) copolymer with
a proportion of the vinylic groups of the copolymer saturated
by the inclusion of a modified group substantially stable to
elimination during formation of a film of the copolymer. The
proportion of saturated vinylic groups controls the extent of
conjugation and thus modulates the semiconductor
bandgap of the copolymer.

Preferably polymers for use in the present invention are
capable of being processed either as precursors which are
subsequently converted to a conjugated form or as
intrinsically soluble polymers. In this regard reference is
made to PCT/WO90/13148, the contents of which are herein
incorporated by reference.

The invention also provides a method of making an
electroluminescent device comprising the following steps:
providing a first charge carrier injecting layer for injecting
positive charge carriers; depositing on said charge carrier
injecting layer a first layer of a soluble polymer in a
solution of a first solvent and to a first predetermined
thickness; depositing a second layer of polymer in the form of
a precursor in a solution of a second solvent to a second

predetermined thickness; heat treating the device so that the
precursor is converted to its polymer which is insoluble; and
depositing a second charge carrier injecting layer for
injecting negative charge carriers, wherein the first and
second predetermined thicknesses are selected so that at least
a part of each of the first and second layers is located in an
emission zone of the device.

Reference is made to our copending application filed on even
date entitled "Manufacture of Electroluminescent Devices"
(Page White & Farrer Ref. 74148/VRD), the content of which are
incorporated herein by reference.

For a better understanding of the present invention and to
show how the same may be carried into effect, reference will
now be made by way of example to the accompanying drawings.

Brief description of the drawings

Figures 1a, 1b and 1c show the chemical structures of a)
PPV, b) a copolymer of PPV and PDMeOPV, c) MEHPPV;
Figure 2a shows the current density against electric
field characteristics of each of four devices on a log-log
scale;
Figure 2b shows current density against voltage on a
linear scale;
Figures 3a to 3d show diagrammatically the structures of
four electroluminescent devices I to IV; and
Figure 4 shows the electroluminescent emission spectra
(all normalised to a peak emission of 1 and offset) of (a)
sample I, (b) sample II, (c) sample III, (d) sample IV, (e) a
unilayer copolymer electroluminescent device, (f) a unilayer
PPV electroluminescent device, (g) to (i) the absorption
spectra of the polymers a,b, and c themselves. Curve g
corresponds to polymer c) MEHPPV; curve h corresponds to
polymer a) PPV and curve i corresponds to copolymer b).

Description of the preferred embodiment

Three different semiconducting poly(arylenevinylene)s are used
to demonstrate the invention.

(a)   (Figure 1a) Poly(p-phenylenevinylene), PPV, was
processed from a tetrahydrothiophenium (THT)-leaving precursor
polymer which is soluble in methanol, PPV has a $\pi - \pi^*$ band
gap of about 2.5eV.

(b)   (Figure 1b) A copolymer was prepared from a
statistical precursor copolymer to PPV and poly(2,5-dimethoxy-
p-phenylenevinylene), PDMeOPV, which is soluble in methanol.
The monomer feed ratio was 9:1. The synthesis of such a
copolymer is described for example in a paper entitled "LEDs
based on Conjugated Polymers: Control of Colour and Efficiency
by P. Burn, et al given at MRS Boston 1991 and published in
Mat. Res. Soc. Symp. 1992 247, 647-654. Under the
experimental conditions used here, the band gap of the polymer
obtained after thermal conversion is blue-shifted with respect
to PPV due to the presence of non-eliminated methoxy groups at
the vinylic carbons adjacent to the dialkoxy-substituted
phenylenes. The resulting copolymer has a $\pi - \pi^*$ band gap of
about 2.6eV.

(c)   (Figure 1c) The third polymer used was
poly(2-methoxy-5-(2-ethylhexloxy)-1,4-phenylenevinylene),
MEHPPV. Due to the long alkyl side-groups this derivative of
PPV is soluble in and processed from chloroform. It has a
$\pi - \pi^*$ band gap of about 2.2eV.

Both the THT-leaving group precursors to PPV and the copolymer
are such they can be laid down by spin coating in solution of
a solvent, which when dry, forms a stable layer onto which a
further layer may be put down. This enables the construction
of multilayer structures since, once a layer has dried,
subsequent deposition of additional polymer layers will not
remove the initial layer. The two THT-leaving group precursor
polymers are insoluble in chloroform, but soluble in
methanol. MEHPPV is soluble in chloroform, but insoluble in
methanol. This difference in solvents allows a layer of

precursor to be spin-coated on top of a layer of MEHPPV
without removal of the MEHPPV and vice-versa. Hence
multilayer structures composed of the three different polymers
were fabricated.

The multilayer devices of conjugated polymers were constructed
as follows. Indium-tin oxide (ITO)-coated glass substrates
were thoroughly cleaned with acetone and subsequently with
propan-2-ol, both in an ultrasonic bath. Multilayer
structures were formed by spin-coating layers of polymer or
precursor, one on top of another as discussed above. All
layers were spin-coated within a nitrogen-filled glovebox
(O_2 and H_2O content 10ppm), in which all subsequent
processing steps were also performed. Film thicknesses of the
polymer layers were set by control of both spin-speed and
solution concentration as follows: the copolymer at 20nm,
MEHPPV at 50nm and PPV at more than 50nm. The thicknesses of
the individual polymer layers and total polymer layer were
measured with a Dektak IIA surface profiler. The samples were
thermally converted at $200^{\circ}C$ in vacuo (10^{-6} torr) for 12
hours to convert the precursor polymers. Calcium contacts
were vacuum deposited on the samples and the samples were
hermetically sealed. Sample areas were 1 mm^2. Four
multilayer device structures have been studied here; details
of construction are summarised in table 1 and illustrated in
Figures 3a to 3d.

To form device I illustrated in Figure 3a, an indium-tin oxide
coated glass substrate 1 was spin coated firstly with a
precursor to the copolymer (b) at a thickness of 20nm (layer
21). The layer was allowed to dry and then a precursor to PPV
(a) in the thickness of 230nm (layer 22) was laid down by spin
coating, and allowed to dry. Finally a layer 23 of MEHPPV (c)
in the thickness of 50nm was laid down by spin coating.
Layers 21 and 22 were put down in a solution of methanol and
layer 23 was put down in a solution of chloroform. The sample
was then heat treated to cause thermal conversion of the
precursors to the copolymer in layer 21 and to PPV in layer

22.   Finally a calcium contact 2 was vacuum deposited on layer
23.

Device II as illustrated in Figure 3b was formed as follows.
Onto an indium-tin oxide coated glass substrate 1 there was
spin coated a first layer 31 of MEHPPV in the thickness of
50nm which was allowed to dry, and then a precursor to PPV 32
in the thickness of 50nm and allowed to dry. Then a precursor
to the copolymer 33 was laid down by spin coating in the
thickness of 20nm. The first layer 31 was put down in a
solution of chloroform and the second and third layers 32,33
were put down in a solution of methanol. The device was heat
treated to thermally convert the precursors in layers 32 and
33 to the respective polymers PPV and the copolymer and a
calcium contact 2 was then vacuum deposited onto layer 33.

Device III illustrated in Figure 3c was formed as follows.
Onto an indium-tin oxide coated glass substrate 1 was spin
coated a first layer 41 of a precursor to the copolymer in a
thickness of 20nm. The precursor was allowed to dry. A
second layer 42 of MEHPPV is laid down by spin coating in the
thickness of 50nm and allowed to dry and then a third layer 43
of the precursor to PPV is laid down by spin coating in a
thickness of 150nm. After this layer had dried a fourth layer
44 of a precursor to the copolymer was laid down by spin
coating in a thickness of 20nm. The device was then heat
treated to thermally convert the precursors to their
respective conjugated polymers and a calcium contact 2 was
vacuum deposited onto layer 44.

Device IV illustrated in Figure 3d was formed as follows.
Onto an indium-tin oxide coated glass substrate 1 was spin
coated a precursor 51 to the copolymer in the thickness of
20nm. This was then allowed to dry. A precursor to PPV 52
was laid down by spin coating in a thickness of 30nm and
allowed to dry and then a precursor to the copolymer 53 was
laid down by spin coating in the thickness of 20nm. The

sample was then heat treated and a calcium contact 2 was
vacuum deposited onto the third layer 53.

In these structures, the calcium contact 2 serves as a cathode
for injecting negative charge carriers and the indium-tin
oxide serves as an anode for injecting positive charge
carriers. Reference numeral 4 indicates a negative contact
and reference numeral 6 indicates a positive contact.

In devices II, III and IV the layer adjacent the calcium
contact 2 is a layer of the copolymer which, after heat
treatment, is insoluble in common solvents. This layer acts
as a barrier layer to shield the cathode from chemical attack,
while allowing the injection of charge carrier into the
emissive region. This layer of copolymer also serves to
resist the diffusion of mobile ions released from the reactive
cathode through the polymer layer. It also provides the
device with strength, mechanical rigidity and stability at
high temperatures. Furthermore, it protects the soluble
polymer (MEHPPV) so that the desirable properties of MEHPPV
such as the required colour or high efficiency for
luminescence can be exploited. Other conjugated polymers or
other polymers which can be used as barrier layers instead of
that illustrated in Figure 1b are methoxy-substituted
precursor polymers to PPV, dimethoxy-PPV, dimethyl-PPV,
polyaniline and derivatives, polyvinylcarbazole, blends of
dimethyl-PPV and any other higher band gap polymers.

As explained above, the indium-tin oxide coated glass
substrate serves as an anode for the device while the calcium
contact 2 serves as a cathode. These constitute means for
enabling an electric field to be applied across the layers.

The devices were driven by applying a positive bias to the ITO
with a Keithley 230 voltage source and electric currents were
monitored with a Keithley 195A multimeter.
Electroluminescence (EL) was observed through the ITO
substrate. Integrated light output was monitored with a

large-area calibrated silicon photodiode in photoamperic mode,
measuring the photocurrent as a voltage across a 1MΩ
resistor. Spectrally-resolved EL measurements were made using
a Coderg PH1 double monochromator and a Hamamatsu R943-02
photomultiplier tube. Internal quantum efficiencies, defined
here as photons generated per injected charge, were measured
at a device brightness of about $5cd/m^2$. In calculating the
internal quantum efficiency account has been taken of the
effects of refraction by the glass substrate, as discussed in
an article in the 1992 issue of Synthetic Metals authored by
Brown, et al. UV/vis absorption spectra were recorded with a
Perkin Elmer λ9 spectrophotometer on samples of polymer
spin-coated on silica substrates.

The four device configurations show colours of emission from
red to yellow/green. Electrical and electro-optical
characteristics for these devices are shown in Table 1, and in
Figures 2a, 2b and 4. In Table V, the layers are denoted in
numerical order from the ITO content 1. In Figures 2a and 2b
note that different thicknesses of the combined polymer layers
give different drive voltages, but that these scale to give a
universal curve for current density versus electric field.
Figure 2b shows the current density against electric field
voltage characteristics of the four devices. Figure 4 shows
the emission spectra from the various devices (the spectra are
offset and normalised to give equal peak heights at the peak
emission wavelengths). Also displayed are emission spectra
from unilayer devices of PPV and the copolymer. The
absorption spectra of the 3 polymers are also shown (curves
g,h,i) (normalised to give a peak $\pi - \pi *$ absorption
coefficient of 1), showing the differing optical band gaps.

Figures 2a and 2b show clearly that the current density under
forward bias is determined primarily by the electric field
(calculated as the applied voltage divided by the sum of the
individual layer thicknesses). In contrast to the results
obtained for the devices formed with PPV and the butyl
PBD/PMMA layers (discussed in the reference referred to above

by P.L. Burn et al), the devices studied here do not show a
large build-up of space charge at the interfaces between
polymer layers. Also, the small differences in band gap for
the polymers in contact with the metal electrode layers do not
affect significantly the threshold fields for charge injection.

The various structures give a range of different emission
colours, and by analysing these it can be identified which of
the polymer layers are acting as sites for radiative decay of
excitons:

Structure I was the only structure to show an emission
spectrum characteristic of a single polymer layer, in this
case MEHPPV. There is no contribution to the emission
spectrum from excitons decaying in the PPV or copolymer
layers, since at energies about 2.35eV there is no emission,
whereas the emission spectra of PPV and copolymer both have
strong emission intensities at 2.35eV. Probably therefore
electron injection is the limiting process in the devices, so
that electron and holes meet in a recombination zone adjacent
to the electron-injecting calcium contact 2. It is
unfavourable for the excitons formed in the MEHPPV layer to
migrate into the other polymer layers which have larger band
gaps. By the same argument, the absence of any contribution
to the emission spectra from the PPV layer indicates that no
electron-hole capture occurs in this layer and thus that no
electrons migrate into the PPV layer through the MEHPPV layer,
under the influence of the electric field. The copolymer and
PPV layers are acting as hole transport layers. The emission
spectra also demonstrate that, surprisingly, the thermal
conversion process does not damage or alter the MEHPPV.

Structure II has the same combination of polymer layers
as structure I but constructed the other way up. The emission
spectrum of the device is broad with emission stretching from
below 1.55eV to above 2.5eV. At 1.75eV, both PPV and
copolymer have negligible emission yet the emission of sample
II is still more than 15% of the peak emission and must be due
to the radiative decay of excitons located in the MEHPPV

layer. Similarly, at 2.35eV MEHPPV has zero emission, yet the
emission of sample II is still more than 30% of the peak
emission for the sample and so the emission at this energy
must be due to the decay of excitons located in either the
copolymer or PPV layers. This device is thus clearly an
example of a conjugated polymer device emitting from more than
one polymer layer. The nature of the generation of the
excitons in the various polymer layers will be discussed later.

Structure III has an emission spectrum very similar to
that for structure II. Thus the emission of this device, for
the same reasons as discussed above, has contributions from
the decay of excitons located in the MEHPPV layer and at least
one of either the PPV or the copolymer layers. It appears the
additional copolymer layer has negligible effect on the
emission spectrum, and one might deduce that no excitons
indeed are located in this additional copolymer layer adjacent
to the ITO. This device also is an example where exciton
decay occurs within the bulk of a polymer multilayer device as
the MEHPPV is separated from both contacts by other layers.

Structure IV has an emission spectrum with contributions
from both the PPV layer and the copolymer layer. The emission
spectrum shows phonon structure at 2.07, 2.26 and 2.39eV which
is less pronounced than that for PPV, though clearer than in
the copolymer.

These devices operate by electron and hole injection at
negative and positive electrodes, with electron-hole capture
to form excitons, which can then decay radiatively. There are
no large changes in the current density-electric field
characteristics accompanying the introduction of several
layers of polymer, so there is probably little or no charge
confinement resulting in space charge build-up at the
interfaces between these layers. Thus there is little
modification of the internal electric field and the conditions
for charge injection and charge migration are not much

affected by the presence of several layers of polymer with similar band gaps.

In structures II-IV emission in several polymer layers can be observed with an emission zone more than 50nm in total thickness. It is of interest to identify the mobile species which gives rise to this wide emission zone. The two candidate mobile species are (i) charge carriers and (ii) neutral excitons. Depending on the behaviour of these charged and neutral species, we can expect to see behaviour ranging from the limit where a broad electron-hole capture zone is narrow, but in which exciton diffusion acts to produce a broad emission zone.

Thus, the precise thicknesses and arrangement of the layers of conjugated polymer within an electroluminescent device can be ascertained from a knowledge of the polymer band gap, electron-hole mobilities in the polymer, and a value for the exciton diffusion lifetime with reference to the models discussed herein. Firstly these cases are outlined by two simple models to give estimates of the widths produced by the two mechanisms.

(i) Width of electron-hole capture zone.

Let us consider that electron hole capture is mediated by Coulombic attraction and will occur within a sphere of radius, $r_{capture}$, where this attraction exceeds the thermal energy. Then

$$kT = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r_{capture}}$$

$$\therefore r_{capture} \le \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT}$$

Taking a value for the relative permittivity ϵ_r of about 4, we have at room temperature $r_{capture} \approx 14nm$. It can be demonstrated from simple models for the drift of charges through the device that, in the absence of barriers for carrier transport at interfaces, the space charge densities of positive and negative charge carriers are low, and that the width of the electron-hole capture zone can be modelled to lie in the range of the polymer layer thicknesses used for example II to IV. At an electric field, F, with a current density, j, and a carrier mobility, μ, the carrier density, p is given by

$$p = j/ev = j/eF\mu$$

Taking typical device operation values of $j = 1 \ mA/cm^2$, and $F = 10^8$ V/m and assuming a mobility, $\mu - 10^{-4} cm^2/V \cdot sec$, as has been observed in similar conjugated polymers for the majority, p-type carriers gives a carrier density, $p = 6.2 \times 10^{20} m^{-3}$. This gives a carrier-carrier separation of about 120 nm.

If electrons have a mobility, μ_n, the number of collisions an electron undergoes in time, t, is $tF(\mu_n + \mu_p)p\sigma$ where σ is the collision cross-section. Assuming every collision results in capture, we can then estimate an electron-hole capture zone width, W_{e-h} given by

$$W_{e-h} = \frac{\mu_n}{(\mu_n + \mu_p)p\sigma} = \frac{\mu_n\mu_p eF}{(\mu_n + \mu_p)j\sigma} = \frac{\mu_n}{(\mu_n + \mu_p)pr_{capture}^2}$$

Using the values here, based on the hole mobilities estimated above, and assuming equal electron and hole mobilities, we find a value of $W_{e-h} \approx 4000$ nm. This width is very much larger than we find here, and we consider that confinement to much smaller thicknesses near the cathode results from a much lower electron mobility.

(ii) Exciton diffusion length.

We may assume a simple exciton diffusion equation, with a
characteristic variance of the displacement from the origin,
$l^2 \sim D\tau$. Exciton lifetimes, τ, of above 0.25 ns have been
measured in PPV. Typical values of the magnitude of diffusion
coefficients, D, in molecular semiconductors are of the order
1×10^{-3} $cm^2 s^{-1}$ and the coefficient in these conjugated
polymers does not exceed this. These values then give an
estimate of the diffusion length of an exciton, $l, \sim 5$ nm.

Although the multilayer emission is observed only in
structures II-IV, it is constructive to consider an analysis
of structure I first. As the emission spectrum of structure I
is characteristic of the single polymer layer of MEHPPV, the
recombination zone is probably confined within the 50 nm
thickness of the MEHPPV layer. From the above analysis, such
a zone thickness would only be consistent with electron-hole
capture by a Coulomb interaction if the electron mobility is
less than $10^{-6} cm^2/V$ sec. This may be the case, since
minority carrier mobilities in organic semiconductors are
often significantly smaller than those of the majority
carriers. Another explanation is that there is a barrier
against electron migration from the MEHPPV layer into the PPV
layer and so confining the recombination zone to the MEHPPV
layer.

As has already been indicated, in structures II-IV the
spectral shifts indicate that emission occurs in layers not
solely adjacent to the calcium contact. In the scenario in
which the width of the emissive layer is determined by the
width of the electron-hole capture zone, there is no barrier
against electron migration in all these structures since
electrons pass from PPV into MEHPPV. The electron-hole
capture zone then extends through several polymer layers and
over more than 200 nm in structure III. Excitons are then
formed in several different polymer layers and then
radiatively decay in several polymer layers, given the

observed emission spectra. Thus, in structure I the
recombination zone is within 50 nm of the electron-injecting
contact, observing emission from only one layer. The
recombination zone is probably limited in this structure due
to a barrier against electron migration out of the MEHPPV
layer.

Though the inventors consider that the width of the
characteristic emissive zone in these EL devices is in part
determined by the statistics for electron-hole capture, there
are other possible explanations. One such is that the
recombination could be occurring within a 50 nm zone adjacent
to the calcium contact (as in structure I) and that there is
subsequent exciton transfer from the recombination zone to
different emission zones. This transfer could occur by
several mechanisms. Firstly, there may be absorption and
re-emission at a longer wavelength, but this is not
significant for the devices studied here. One reason for this
is that one would expect to see a concomitant fall-off in
device efficiency, given that luminescence yields are not
100%. Experimentally, there is little variation in efficiency
from one device to another, as summarised in table 1.

Secondly, there may be exciton diffusion from one layer to
another. The radiative lifetimes for singlet excitons in PPV
are of the order of 1 nsec. Measured photoluminescence
lifetimes are lower, indicating that there are competing
non-radiative decay mechanisms, but lifetimes are 250 psecs or
longer at room temperature, and this allows for diffusion of
the exciton through the polymer prior to decay. Evidence for
migration of excitons, created by photoexcitation, within a
film of PPV, is provided by comparison of absorption and
photoluminescence spectra. Even in polymer samples that show
a considerable spread in intra-chain conjugation length, and
hence band gap, such that the phonon structure expected in the
absorption spectrum is washed out, the luminescence spectra
show clear vibronic structure, indicating that the excitons so
formed, prior to emission, have migrated to the chain segments

with longest uninterrupted conjugation length and hence with
lower band gap. Exciton diffusion is very well studied in
molecular semiconductors and under the conditions in these
conjugated polymer films may occur either by direct hopping or
by Förster transfer. Energy transfer to a chromophore with a
longer wavelength of emission, which can be selectively
introduced as a dopant in the semiconductor, is a well-studied
phenomenon.

A further example of the invention is discussed below. A
different soluble conjugated polymer is used in place of the
MEH-PPV. The polymer used is poly(3-dodecylthienylene), P3DT,
for which the chemical structure is
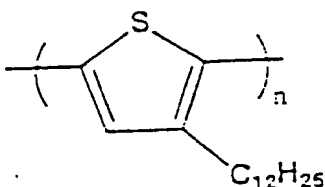
This polymer is soluble by virtue of the dodecyl side-chain,
and is processed from solution, in for example, chloroform.
It shows good photoluminescence and has been shown to function
in an electroluminescent device.

A device was fabricated in a similar manner to Example II,
with a layer of P3DT (thickness 500 nm) on the ITO contact 1,
and a layer of PPV precursor spin-coated on top to a thickness
of 100nm and subsequently heated to convert to PPV (200°C,
12 hours) in place of the two precursor-route layers in
Example II. Calcium was evaporated onto this as a final stage.

While these particular thicknesses were found to be
successful, it is desirable to have a thickness of less than
500nm for P3DT. This is acceptable provided that at least
part of both of the layers lie in the emission zone of the
device.

This device shows a high threshold voltage for charge
injection, requiring 80 V or more to give readily visible

emission. This high drive voltage is due to the considerable
thickness of the P3DT layer. The quantum efficiency for this
device was found to be about 0.08%.

The light output was observed by eye to be deep red,
characteristic of the luminescence of P3DT which is
considerably to the red of PPV. Emission from the PPV layer
viewed through the P3DT layer and the ITO/glass substrate
would be strongly attenuated by the absorption of the PPV
emission by the P3DT (the PPV emission falls in the absorption
band of P3DT since this has a lower band gap).

This device demonstrates various points:

(i) Emission is produced in a layer not immediately adjacent
to the cathode. It can reasonably be expected that emission
was also observed from the PPV layer, (c.f Example II). This
is therefore another example of a multilayer emitting device,
but should optimally be modified so that the polymer layer
thicknesses avoid the problem of absorption by one layer of
the light produced by another.

(ii) Furthermore, it is a device where a layer of precursor
polymer has successfully been laid down onto a soluble polymer
layer, taking advantage of the different solubilities of the
polymers, and where the structure survives the thermal
treatment required to convert to the conjugated form.

Industrial Application

In summary, the inventors have discovered that multilayer
electroluminescent devices with emission from more than one
layer can be fabricated. Such multilayer structures could be.
used to control device characteristics in a range of
applications. For example at least two polymer layers can be
arranged to be simultaneously luminescing. This will allow
generation of a broader spectrum than can be achieved with a

single layer (see structures II, III and IV), and may allow
fabrication of a white-light source.

A particularly important discovery is that the region of the
device in which the emission occurs can be arranged to be
sufficiently wide so that several polymer layers can
simultaneously emit. The probable reasons for this are
firstly, that in the absence of charge trapping at an
interface between two polymer layers, the electron-hole
capture process requires thicknesses of polymer of at least 50
nanometers so that excitons are formed in the region of this
thickness. Secondly, excitons once formed will diffuse before
they decay and this process of diffusion can further broaden
the width of the emission zone. The inventors have determined
that for optimum performance the device should be manufactured
so as to take into account the following points. As is
evident from the examples, the emission is usually to be seen
from the region of the polymer adjacent the cathode. This
indicates that either electron injection is more difficult
than hole injection and/or that electrons have lower mobility
than holes. Emission from more than one layer is therefore
more likely to be achieved in devices where appropriate layers
are deposited close to the cathode. Another determinative
feature is the band gap of the polymer layers. Inappropriate
ordering of the polymer layers can result in complete trapping
of excitons within one layer only as seen in Example 1 in
which there is a low band gap polymer (MEHPPV) adjacent the
cathode. Thus, preferably, the band gaps are ordered to
assist charge carrier transfer and capture.

Sample Number	I	II	III	IV
Layer 1 thickness (nm)	copolymer 20	MEHPPV 50	copolymer 20	copolymer 20
Layer 2 thickness (nm)	PPV 230	PPV 50	MEHPPV 50	PPV 30
Layer 3 thickness (nm)	MEHPPV 50	copolymer 20	PPV 150	copolymer 20
Layer 4 thickness (nm)			copolymer 20	
Colour of light emission	red	orange	orange	yellow
Quantum efficiency, η (%)	0.30	0.23	0.24	0.16
Electric field (V/cm) required to produce:				
1 mA cm^{-2}	8.0×10^5	7.1×10^5	7.4×10^5	7.1×10^5
2 mA cm^{-2}	8.6×10^5	7.7×10^5	7.9×10^5	7.7×10^5

Table 1. Characteristics of the four multilayer electroluminescent devices. Polymer layer 1 was spin-coated directly on top of the ITO contact. The calcium contact was evaporated on top of polymer layer 3 (or polymer layer 4 in the case of device III).

CLAIMS:

1.   An electroluminescent device comprising:
      a first charge carrier injecting layer for injecting
positive charge carriers;
      a first layer of a semiconductive conjugated polymer
having a band gap selected such that when it is excited
radiation at a first wavelength is emitted;
      a second layer of a semiconductive conjugated polymer
having a band gap selected such that when it is excited
radiation at a second wavelength is emitted;
      a second charge carrier injecting layer for injecting
negative charge carriers; and
      means to enable an electric field to be applied across
the said layers wherein at least a part of each of the first
and second layers is located in an emission zone of the
device, said emission zone extending over a capture region of
the device wherein positive and negative charge carriers
combine with one another to form excitons and having a width
characteristic of the distance over which said excitons
migrate before decaying radiatively, such that on application
of an electric field to the device both of said first and
second polymer layers are caused to emit radiation at their
respective wavelengths.

2.   An electroluminescent device as claimed in claim 1
wherein the width of the emission zone is not greater than
200nm.

3.   An electroluminescent device as claimed in claim 1 or 2
wherein the first layer has a thickness which is not greater
than 50nm.

4.   An electroluminescent device as claimed in claim 1 or 2
wherein there is a third layer of a semiconductive conjugated
polymer between said second polymer layer and said second
charge carrier injecting layer.

5.   An electroluminescent device as claimed in claim 4
wherein the third layer has a thickness not greater than 50nm.

6.   An electroluminescent device as claimed in claim 4 or 5
wherein the third layer constitutes a barrier layer adjacent
the second charge carrier injecting layer.

7.   An electroluminescent device as claimed in claim 4, 5 or
6 wherein the third layer is light emissive.

8.   An electroluminescent device as claimed in any preceding
claim wherein there is a further polymer layer between the
first layer and the first charge carrier injecting electrodes.

9.   An electroluminescent device as claimed in any preceding
claim wherein the second charge carrier injecting layer is
calcium.

10.   An electroluminescent device as claimed in any preceding
claim wherein the first charge carrier injecting layer is
indium tin oxide.

11.   An electroluminescent device as claimed in any preceding
claim wherein the semiconductive conjugated polymer is
selected from the group comprising poly(p-phenylene vinylene);
substituted derivatives of poly(p-phenylene vinylene); and
copolymers including that polymer.

12.   An electroluminescent device as claimed in any of claims
1 to 10 wherein the first polymer layer is a
poly(2.5-dialkoxyphenylene-vinylene) selected from the group
comprising MEHPPV; poly(2-methoxy-5-(2-methylpentyloxy)-1,
4-phenylenevinylene); poly(2-methoxy-5-pentyloxy-1,4-phenylene-
vinylene); and poly(2-methoxy-5-dodecyloxy-1,4-phenylene-
vinylene).

13.   An electroluminescent device as claimed in any of claims
1 to 12 wherein the second polymer layer is PPV of formula

$$\left[\!\!-\!\!\left\langle \bigcirc \right\rangle\!\!-\!\! CH\!=\!CH\!-\!\right]_{n}$$
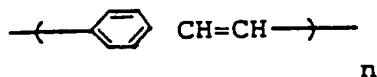
14.   An electroluminescent device as claimed in any of claims
1 to 10 wherein the first polymer layer is selected from the
poly(alkylthienylene)s.

15.   An electroluminescent device as claimed in claim 11
wherein the copolymer is a conjugated poly(arylene vinylene)
copolymer with a proportion of the vinylic groups of the
copolymer saturated by the inclusion of a modifier group
substantially stable to elimination during formation of a film
of the copolymer.

16.   An electroluminescent device as claimed in claim 1
wherein the first layer is a layer of MEHPPV having a
thickness of about 50nm and the second layer is PPV having a
thickness of less than 200nm.

17.   An electroluminescent device as claimed in claim 16 which
includes a barrier layer between the second layer and the
second charge carrier injecting layer having a thickness of
about 20nm.

18.   An electroluminescent device as claimed in claim 1
wherein the first layer is a layer of P3DT having a thickness
of about 500nm and the second layer is PPV having a thickness
of about 100nm.

19.   An electroluminescent device as claimed in claim 4, 5, 6
or 17 wherein the third layer is a copolymer of PPV and
PDMeOPV.

20. A method of making an electroluminescent device
comprising the following steps:

   providing a first charge carrier injecting layer for
injecting positive charge carriers;

   depositing on said charge carrier injecting layer a first
layer of a soluble polymer in a solution of a first solvent
and to a first predetermined thickness;

   depositing a second layer of polymer in the form of a
precursor in a solution of a second solvent to a second
predetermined thickness;

   heat treating the device so that the precursor is
converted to its polymer which is insoluble; and

   depositing a second charge carrier injecting layer for
injecting negative charge carriers, wherein the first and
second predetermined thicknesses are selected so that at least
a part of each of the first and second layers is located in an
emission zone of the device.

21. A method according to claim 20 when used to manufacture a
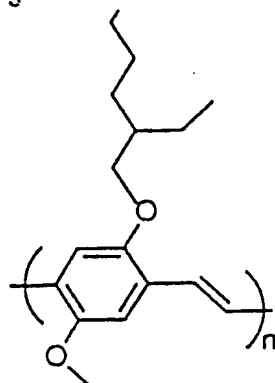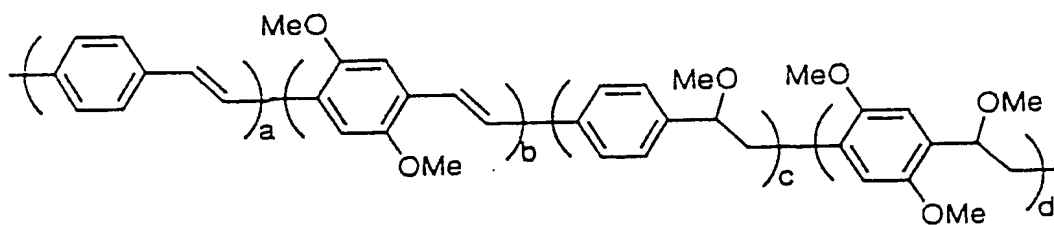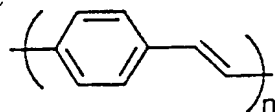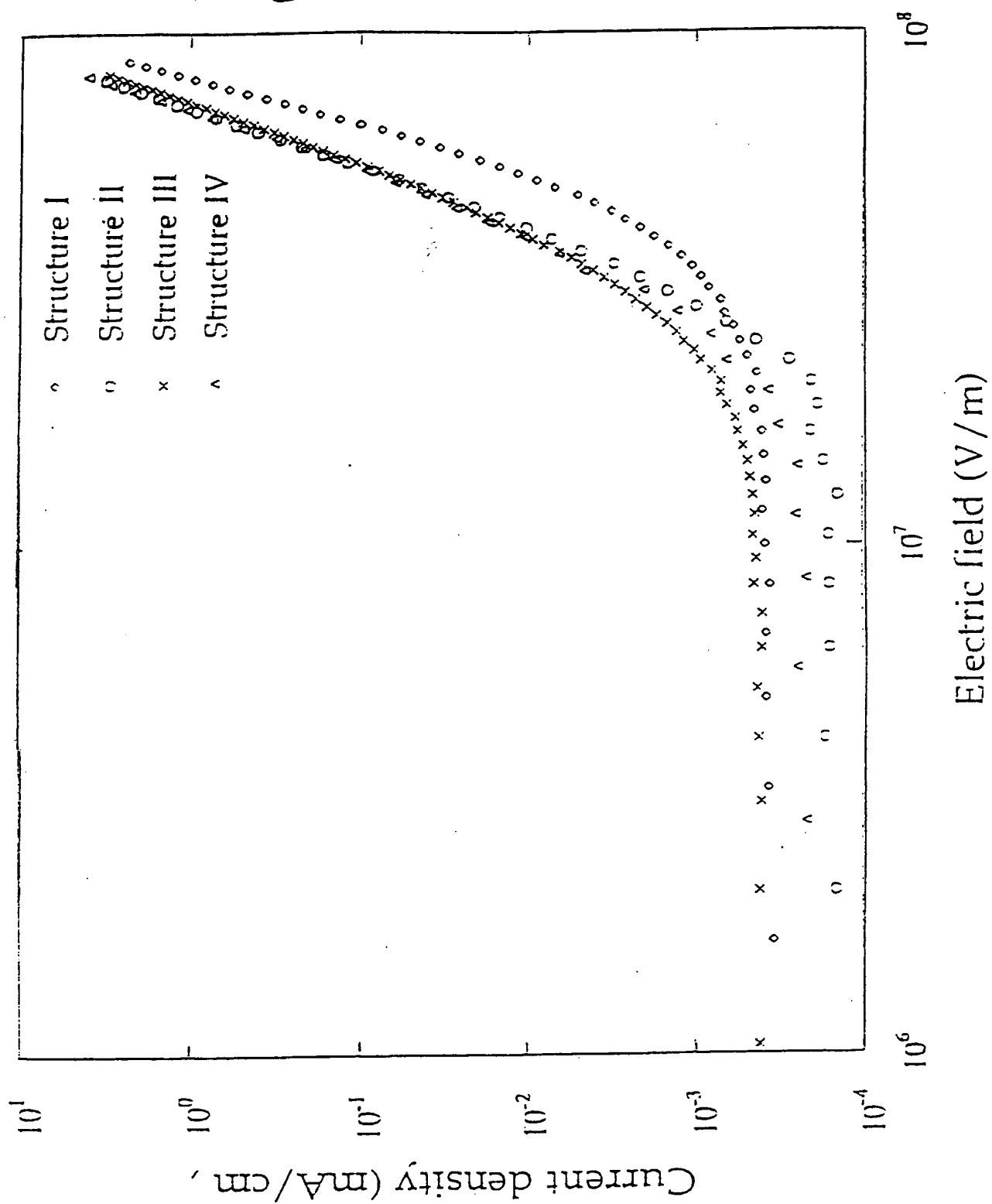device according to any of claims 1 to 19.

Fig. 1c

Fig. 1a

Fig. 1b

Fig. 2a

Fig. 2b

◇ Structure I
○ Structure II
× Structure III
△ Structure IV

4 / 5

Fig 3a

Layer 23
Layer 22
Layer 21
6
1

2
4
ITO
Glass

Fig. 3b

Layer 33
Layer 32
Layer 31
1

2
ITO
Glass

Fig. 3c

Layer 44
Layer 43
Layer 42
Layer 41
1

2
ITO
Glass

Fig. 3d

Layer 53
Layer 52
Layer 51
1

2
ITO
Glass
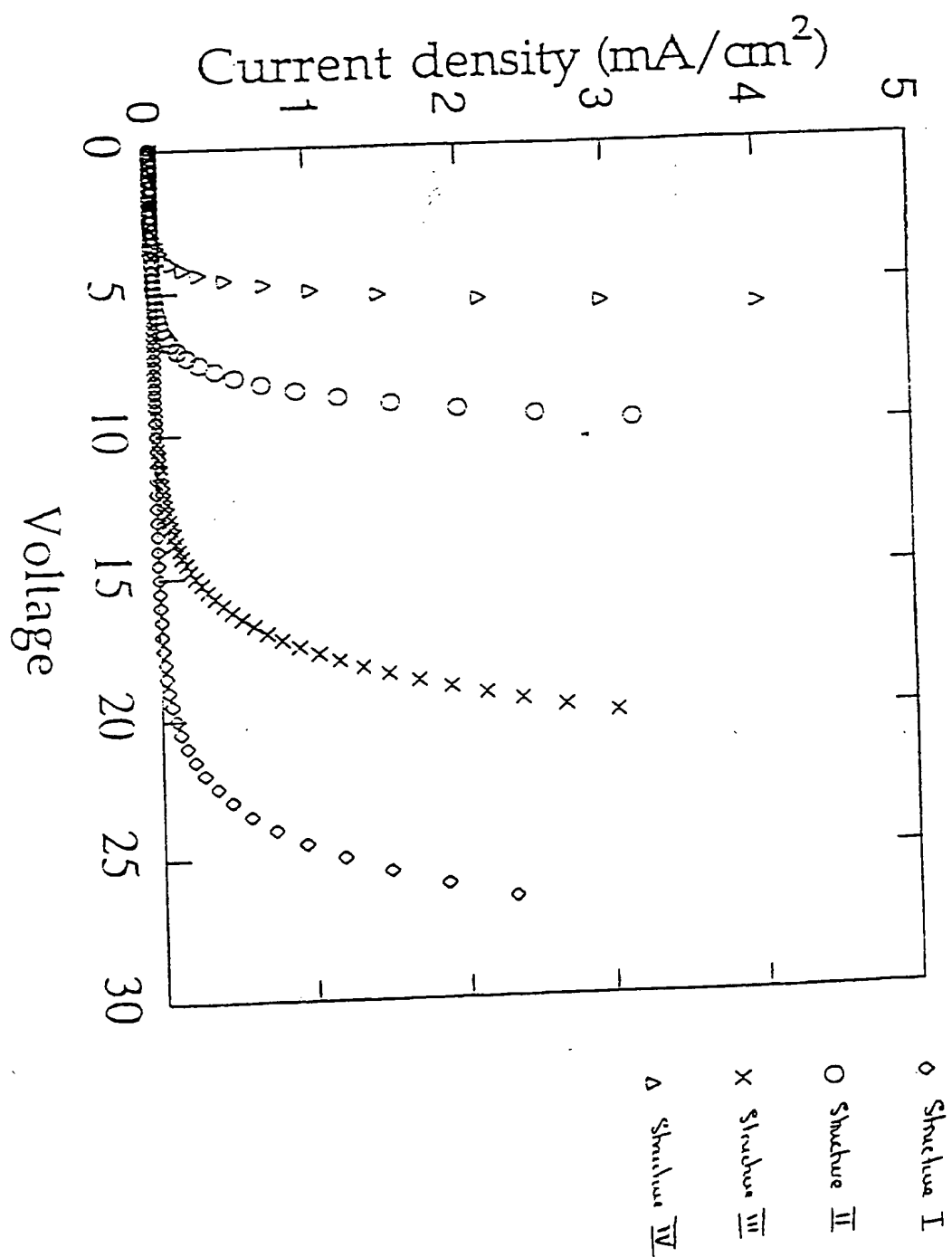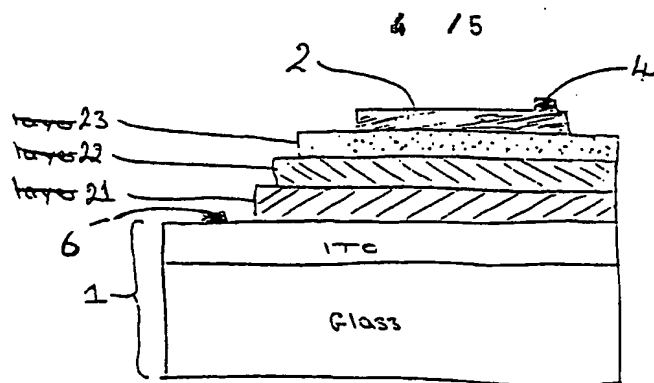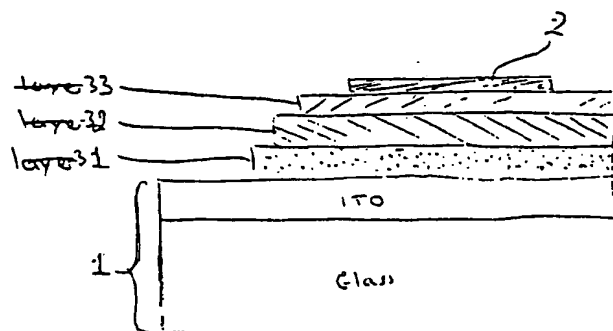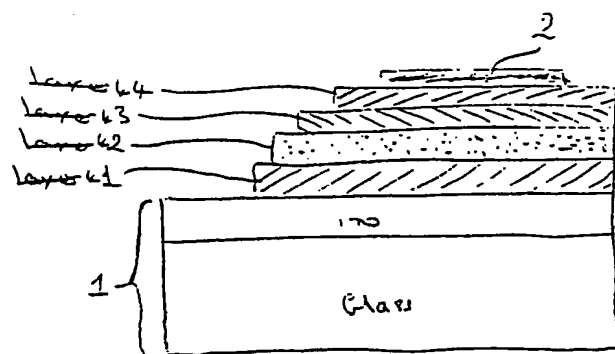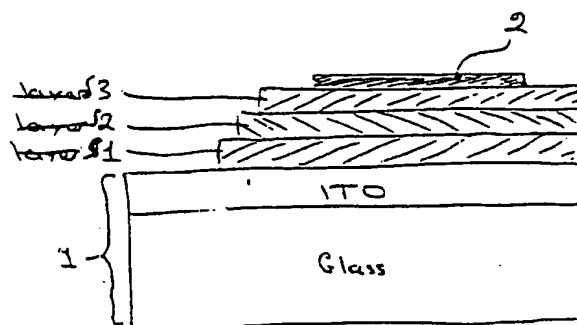
Emission spectra
(normalised and displaced)
(arbitrary units)

Absorption Spectra
(normalised)

Energy (eV)

Fig. 4

I. CLASSIFICATION OF SUBJECT MATTER   (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H05B33/14;   H05B33/10;   C09K11/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]	
Classification System	Classification Symbols
Int.Cl. 5	H05B ; C09K

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document, [11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
E	EP,A,0 553 950 (TOSHIBA) 4 August 1993 see claims 1-14; example 36 ---	1-7,10
A	EP,A,0 443 861 (SUMITOMO) 28 August 1991 cited in the application see claims 1-14 ---	1-3, 11-14
A	EP,A,0 390 551 (TOSHIBA) 3 October 1990 see claims 1-16 ---	1-7,10
A	WO,A,9 203 491 (CAMBRIDGE RESEARCH) 5 March 1992 see claims 1-28 ---	11-13
		-/--

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29 SEPTEMBER 1993	1 9. 10. 93
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	DROUOT M.C.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	WO,A,9 203 490 (CAMBRIDGE RESEARCH) 5 March 1992 cited in the application see claims 1-51 ---	11-13,15
A	WO,A,9 013 148 (CAMBRIDGE RESEARCH) 1 November 1990 cited in the application see claims 1-27 -----	1-3, 11-13

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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		WO-A-	9203490	05-03-92
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		EP-A-	0423283	24-04-91
		JP-T-	4500582	30-01-92

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